

# Synthesis of high performance phenolphthalein-based cardo poly(ether ketone imide)s via aromatic nucleophilic substitution polymerization

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## ABSTRACT

A series of cardo poly(ether ketone imide)s (PEKI-C) containing large-volume bulky phthalide groups were prepared by aromatic nucleophilic substitution reaction of commercially available phenolphthalein and 4,4'-bis(4-fluorophthalimido)diphenyl ether/4,4'-difluorobenzophenone. The glass transition temperatures ( $T_g$ s) increased from 221 to 278 °C with increasing the content of 4,4'-bis(4-fluorophthalimido)diphenyl ether moiety in the copolymerization. The 5% weight loss temperatures ( $T_{5\%}$ ) of PEKI-C (**a–e**) reached up to 472–495 °C in nitrogen and 466–481 °C in air. Flexible films, which could be easily cast from the polymer solutions, exhibited good mechanical properties with tensile strengths of 73–124 MPa, elongations at break of 9.7–12.8%, and tensile moduli of 2.2–2.8 GPa. Their films with cut-off wavelengths from 336 to 368 nm were transparent and essentially colorless. It is noted that the  $T_g$ ,  $T_{5\%}$ , tensile strengths, elongations at break, and tensile moduli of PEKI-C (**a–e**) increased with increasing the content of 4,4'-bis(4-fluorophthalimido)diphenyl ether in the copolymerization.

## 1. Introduction

Polymers containing cyclic side groups in the backbone of macromolecule repeating units are defined as “cardo polymers”, which means loop in Latin, because the pendant cyclic groups are considered as loops of the polymer main chain. Compared with conventional linear polymers without side groups, cardo polymers possess enhanced solubility in common organic solvents, higher glass transition temperature, higher softening temperature, higher transmittance in the visible region as well as excellent mechanical toughness [1,2].

In recent years, phenolphthalein-based cardo polymers have been most widely studied. Phenolphthalein, which is a kind of commercially available industrial product and can easily be synthesized from phenol and phthalic anhydride [3], is a common pharmaceutical raw material and an important acid-base indicator in analytical chemistry. Many high performance polymers with phenolphthalein-based cardo groups have been synthesized, including poly(arylene ether sulfone)s (PES-C) [4–14], poly(arylene

ether ketone)s (PEK-C) [15–21], poly(benzimidazole) [22,23], and poly(etheroxadiazoles) [24]. Among these high performance engineering plastics, PES-C and PEK-C, which possessed good solubility, high glass transition temperature, light-colored and fairly transparent optical properties, good thermal-oxidative stability as well as excellent mechanical toughness, have been industrialized in China and widely used in many applications such as aerospace field, microelectronic area, national defense industry, wire enamels, sterilizable medical equipment, and others [13–15]. The good solubility and transparency of PES-C and PEK-C were attributed to the presence of bulky pendent phthalide groups, which inhibited close packing, thereby increasing the free volume among the molecular chains and reducing the interchain interactions. The high glass transition temperature was also due to the bulky phthalide groups which remarkably improved the rotational energy barrier [13].

Polyimides containing phenolphthalein-based cardo groups were also studied in recent years, especially Yang and coworkers have reported a series of research work on poly(ether imide)s with phthalide cardo groups [25–36]. Compared with conventional linear polyimides, cardo polyimides from phenolphthalein-based tetracarboxylic dianhydrides or phenolphthalein-based diamines have better solubility, higher glass transition temperature and higher transmittance in the visible region. Reddy and coworkers

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synthesized good soluble and thermal stable polyimides from 3,3-bis(4-aminophenyl)-phthalide [37]. Myung also reported a series of polyimides synthesized from phenolphthalein-based diamines which was originated from the Williamson ether condensation reaction between phenolphthalein and 4-chloronitrobenzene [38]. Moreover, Hamciuc studied the dielectric properties of poly(ether imide)s containing phthalide groups synthesized from phenolphthalein-based tetracarboxylic dianhydride which was derived from nitro displacement reaction of 4-nitrophthalonitrile with phenolphthalein in the presence of  $K_2CO_3$  [39]. Recently, Guo studied the solubility, thermal, mechanical and optical properties of polyimide containing phenolphthalein groups synthesized from a novel phenolphthalein-based diamine [40]. In conclusion, the synthetic route of polyimides with phthalide cardo groups was from the polycondensation of either phenolphthalein-based tetracarboxylic dianhydrides or phenolphthalein-based diamines.

As far as we know, it has not been exploited to make cardo poly(ether imide)s by direct aromatic nucleophilic substitution reaction of phenolphthalein and bishalophthalimides. Considering that the introduction of phthalide cardo groups will improve the solubility, thermal and mechanical properties, as well as optical properties. In this paper, we synthesized and characterized a series of poly(ether ketone imide)s with phthalide cardo groups by direct condensation of phenolphthalein and 4,4'-bis(4-fluorophthalimido)diphenyl ether/4,4'-difluorobenzophenone with different molar ratio. The solubility, thermal stability, mechanical properties, rheological properties, as well as optical properties of PEKI-C (**a–e**) were investigated in detail.

## 2. Experimental

### 2.1. Materials

Phenolphthalein (PP) was purchased from Shanghai Chemical Reagent Plant. 4,4'-Difluorobenzophenone was kindly supplied by Nanjing Weixun Chemical Co. and used as received. Pyromellitic dianhydride (PMDA) was purchased from Aladdin Chemical Reagent Plant and used as received without further purification. 4,4'-Diaminodiphenyl ether (4,4'-ODA) was purchased from Shandong Wanda Chemical Company. *N*-phenyl-4-fluorophthalimide (4-FPI) was synthesized in our laboratory according to the literature [41]. *N,N*-Dimethylacetamide (DMAc), *N*-methyl-2-pyrrolidone (NMP), sulfolane, toluene, and xylene were purified by distillation over calcium hydride and stored over 4 Å molecular sieves. All other reagents for the study were commercially obtained and used as received without further purification.

### 2.2. Measurements

The Fourier transform infrared spectra (FT-IR) were obtained from a Thermo Nicolet 6700 FT-IR spectrometer, the sample was prepared with KBr pellets. The  $^1H$  and  $^{13}C$  NMR spectra were measured at 400 MHz on a Bruker 400 AVANCE III spectrometer, using  $CDCl_3$  or dimethyl sulfoxide- $d_6$  (DMSO- $d_6$ ) as solvents. The inherent viscosities ( $\eta_{inh}$ s) were measured with an Ubbelohde viscometer at  $30 \pm 0.1$  °C in DMAc at a concentration of 0.5 g/dL. Thermogravimetric analysis (TGA) was obtained from a Perkin–Elmer Diamond TG/DTA instrument at a heating rate of 10 °C/min under nitrogen and air atmosphere (flow rate of 50 mL/min). Differential scanning calorimetry (DSC) was carried out on a Mettler Toledo DSC at a heating rate of 20 °C/min under nitrogen atmosphere with 50 mL/min gas flow, and  $T_g$  was obtained at the middle of the thermal transition from the second heating. The tensile measurements were tested at least six PI film specimens (50 mm long, 10 mm wide, and about 0.03 mm thick) by an Instron

model 5567 at room temperature, and the results were averaged scan. Dynamic mechanical thermal analysis (DMTA) was prepared on PI film samples (20 mm long, 5 mm wide, and about 0.02 mm thick) on a Mettler Toledo DMA at a heating of 3 °C/min from 30 to 300 °C with a load frequency of 1 Hz in air. The wide-angle X-ray diffraction (WAXRD) measurements were conducted on a Bruker D8 Advance with Cu  $K\alpha$  radiation, at a scanning rate of 5°/min ( $2\theta = 5–50^\circ$ ), operated at 40 kV and 40 mA. The melt flow property of polyimides was performed on an SRZ 400E molten index instrument (Changchun intelligent instrument equipment co., Ltd). Melt index (MI) was detected by melting a sample with maintaining at 330 °C for 2 min and measuring under a load of 12.5 kg. Elemental analyses were carried out on a Perkin–Elmer model 2400II C, H, N analyzer. The rheological properties of polyimides were performed on a rotational Physica MCR 301 rheometer (Anton Paar, Austria) in an oscillation model with air flow. The number average molecular weight ( $M_n$ ), weight average molecular weight ( $M_w$ ) and polydispersity ( $M_w/M_n$ ) were determined by gel permeation chromatography (GPC) (HLC-8320GPC EcoSEC, Tosoh) with polystyrene calibration using  $CHCl_3$  as the eluent with a flow rate of 1.0 mL/min.

### 2.3. Synthesis of monomers 4,4'-bis(4-fluorophthalimido)diphenyl ether

In a 500 mL round-bottomed flask equipped with a magnetic stirrer and a reflux condenser, 4,4'-oxydianiline (ODA) (20.02 g, 0.10 mol) and acetic acid (300 mL) were added. The mixture was heated until ODA was completely dissolved in acetic acid under nitrogen atmosphere. After addition of 4-fluorophthalic anhydride (33.2 g, 0.20 mol), the mixture was refluxed for 12 h, then cooled to room temperature. The light yellow precipitate was collected by filtration, washed with acetic acid, and then dried under vacuum at 150 °C for 12 h. 4,4'-Bis(4-fluorophthalimido)diphenyl ether was obtained at the yield of 89.6% (47.43 g) after recrystallization from toluene/DMAc (v/v = 5:1); m.p. 261–262 °C.  $^1H$  NMR (DMSO- $d_6$ , ppm):  $\delta$  8.07–8.03 (2H, q,  $J = 4.0$  Hz), 7.89–7.87 (2H, dd,  $J_1 = 8.0$  Hz,  $J_2 = 2.0$  Hz), 7.76–7.71 (2H, t,  $J = 8.0$  Hz), 7.51–7.49 (4H, d,  $J = 8.8$  Hz), and 7.25–7.23 ppm (4H, d,  $J = 8.8$  Hz). FT-IR (KBr):  $\nu = 1770$  (asymmetric C=O stretching), 1718 (symmetric C=O stretching), 1385 (C–N stretching), 738  $cm^{-1}$  (C=O bending), and 1251  $cm^{-1}$  (Ar–O–Ar stretching). Elemental analysis for  $C_{28}H_{14}N_2O_5F_2$  (496.42 g/mol): calcd. C, 67.75%; H, 2.84%; N, 5.64%. Found C, 67.93%; H, 2.72%; N, 5.56%.

### 2.4. Synthesis of polymers

The cardo poly(ether ketone imide)s (PEKI-C) were prepared by the solution polycondensation in DMAc. A typical procedure for PEKI-C (**c**) was carried out as follows: to a 50 mL round-bottomed flask equipped with a magnetic stirrer, a nitrogen inlet and a reflux condenser, monomers PP (3.02 g, 0.01 mol), anhydrous  $K_2CO_3$  (1.52 g, 0.011 mol), xylene (20 mL), and freshly distilled DMAc (20 mL) were added. A dark purple solution was formed. When the temperature was raised to 150 °C, water began to be collected in the Dean–Stark trap. After xylene and water were distilled out, 4,4'-difluorobenzophenone (1.09 g, 5.00 mmol) and 4,4'-bis(4-fluorophthalimido)diphenyl ether (2.48 g, 5.00 mmol) were added, the reactant was heated gradually to 160 °C, and allowed to react at this temperature for 12 h to finally obtain a viscous solution. Subsequently, 4-FPI (5.20 mg, 0.02 mmol) was added and reacted for another 2 h to obtain 4-FPI end-capped PEKI-C. Then the solution was cooled to room temperature and carefully poured into 300 mL ethanol with a vigorously stirred magnetic stirrer to yield silky precipitate. The precipitate was filtered, then

washed thoroughly with boiling ethanol for several times, and dried at 120 °C under vacuum for 8 h. The inherent viscosity of PEKI-C (**c**) in DMAc at a concentration of 0.5 g/dL at 30 °C was 0.42 dL/g. FT-IR (KBr,  $\text{cm}^{-1}$ ):  $\nu = 1775$  (asymmetric C=O stretching), 1715 (symmetric C=O stretching), 1652 (Ar-CO-Ar), 1392 (C-N stretching), 732 (C=O imide ring deformation), and 1250  $\text{cm}^{-1}$  (Ar-O-Ar stretching).

Other PEKI-C were synthesized following the typical procedure for PEKI-C (**c**).

PEKI-C (**a**): FT-IR (KBr,  $\text{cm}^{-1}$ ): 1772 (lactone carbonyl), 1650 (Ar-CO-Ar), and 1246  $\text{cm}^{-1}$  (Ar-O-Ar stretching).

PEKI-C (**b**): FT-IR (KBr,  $\text{cm}^{-1}$ ): 1777 (asym C=O stretching), 1718 (sym C=O stretching), 1651 (Ar-CO-Ar), 1380 (C-N stretching), and 1248  $\text{cm}^{-1}$  (Ar-O-Ar stretching).

PEKI-C (**d**): FT-IR (KBr,  $\text{cm}^{-1}$ ): 1775 (asym C=O stretching), 1716 (sym C=O stretching), 1650 (Ar-CO-Ar), 1386 (C-N stretching), and 1243  $\text{cm}^{-1}$  (Ar-O-Ar stretching).

PEKI-C (**e**): FT-IR (KBr,  $\text{cm}^{-1}$ ): 1779 (asym C=O stretching), 1722 (sym C=O stretching), 1385 (C-N stretching), and 1250  $\text{cm}^{-1}$  (Ar-O-Ar stretching).

## 2.5. Polymer film preparation

The PEKI-C (**a-e**) powders were dissolved in DMAc to give the polymer solution with a solid content of 10%. Then the polymer solutions were casted onto clean glass plates, which were placed in an 80 °C oven for 8 h to volatilize most of solvents. The semidried PI films were further dried by programmed heating at 100 °C for 30 min, 150 °C for 30 min, 200 °C for 30 min, 250 °C for 30 min, 280 °C for 30 min. After natural cooling to room temperature, the films were stripped from the glass plates by immersed in water. The obtained thin films were about 20–30  $\mu\text{m}$  thick, which were used for DMTA and tensile measurements.

## 3. Results and discussion

### 3.1. Monomer synthesis

The 4,4'-bis(4-fluorophthalimido)diphenyl ether was prepared in our laboratory by directly reacting ODA with 4-fluorophthalic anhydride, as shown in Scheme 1. Yellow needle-like crystal monomer was obtained after recrystallization from acetic acid/toluene.  $^1\text{H}$  NMR signals corresponding to the central phenyl groups and the 4-fluorophthalimido groups are given in Fig. 1. Furthermore, the molecular structure of the monomer was also confirmed by IR spectra. The characteristic absorption bands were observed at about 1776 (C=O asymmetric stretching), 1721 (C=O symmetric stretching), 1382 (C-N stretching), and 735  $\text{cm}^{-1}$  (C=O imide ring deformation). All these data proved that the monomer was successfully prepared.

### 3.2. Polymer synthesis

As presented in Scheme 2, a series of PEKI-C (**a-e**) were synthesized via aromatic nucleophilic substitution polymerization. The reaction was conducted in polar aprotic solvent DMAc, using  $\text{K}_2\text{CO}_3$  as the catalyst.

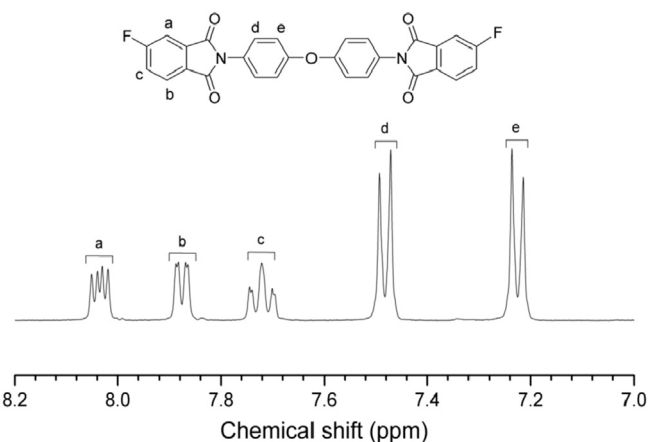


Fig. 1.  $^1\text{H}$  NMR spectra of 4,4'-bis(4-fluorophthalimido)diphenyl ether.

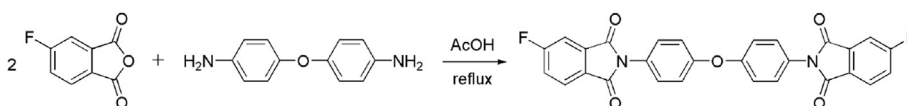
As shown in Table 1, the ratio of 4,4'-difluorobenzophenone to 4,4'-bis(4-fluorophthalimido)diphenyl ether was 1:0, 3:1, 1:1, 1:3 and 0:1, thus the polymers were coded as **a**, **b**, **c**, **d** and **e**, respectively. The structures of PEKI-C (**a-e**) were confirmed by IR spectra, and the characteristic absorption bands around 1775 (asymmetric C=O stretching), 1714 (symmetric C=O stretching), 1392 (C-N stretching) and 735  $\text{cm}^{-1}$  (C=O imide ring deformation) are assigned to the imido ring. The absorption band near 1240  $\text{cm}^{-1}$  can be assigned to the stretching of Ar-O-Ar, which derived from aromatic nucleophilic substitution polymerization of phenolphthalein and 4,4'-bis(4-fluorophthalimido)diphenyl ether/4,4'-difluorobenzophenone.

As shown in Table 1, there were three possible units of linkage (IPI, KPI, KPK) in the polymer chain. As presented in Fig. 2, structural features of the PEKI-C (**a-e**) were confirmed by  $^{13}\text{C}$  NMR spectra. It should be noted that the signal intensity of carbon ( $\text{C}_1, \text{C}_1'$ ) in ketone moiety decreased from **a** to **d**, while the signal intensity of carbon ( $\text{C}_2, \text{C}_3, \text{C}_2', \text{C}_3'$ ) in imide moiety increased from **b** to **e**. This was consistent with the ratio change of 4,4'-difluorobenzophenone to 4,4'-bis(4-fluorophthalimido)diphenyl ether in polymerization. The signal of aliphatic quaternary carbon in phenolphthalein at about 90.73 ppm was always present in all the polymers.

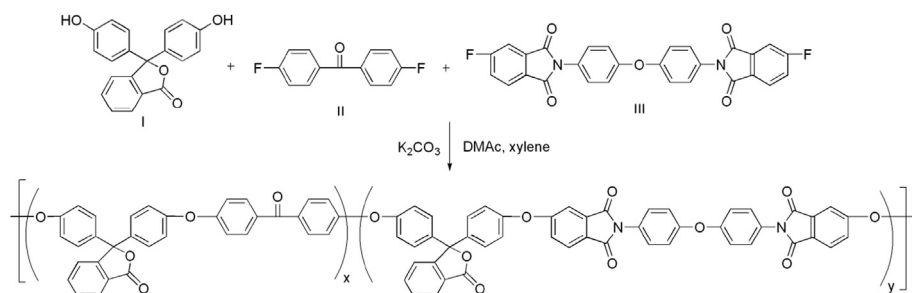
### 3.3. Properties of the PEKI-C (**a-e**)

#### 3.3.1. Solubility

The qualitative solubility of these polymers was investigated in common organic solvents, and the results were summarized in Table 2. The PEKI-C exhibit excellent solubility in ordinary organic solvents, such as *N,N*-dimethylformamide (DMF), *N,N*-dimethylacetamide (DMAc), dimethyl sulfoxide (DMSO), *N*-methyl-2-pyrrolidone (NMP), and *m*-cresol. The good solubility of these cardo polymers could be explained by the presence of bulky cardo phthalide groups, which contribute to create a distance between the macromolecular chains. The disturbed packing of the macromolecular chains facilitates the diffusion of small molecules of solvents into polymer matrix, which leads to good solubility. The



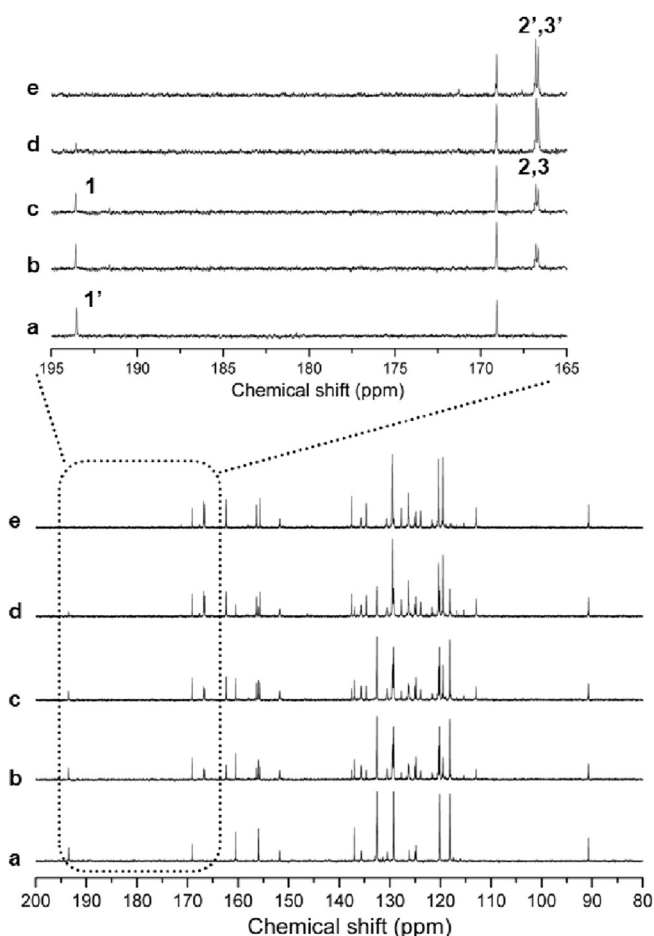
Scheme 1. Synthesis of 4,4'-bis(4-fluorophthalimido)diphenyl ether from 4-fluorophthalic anhydrides and ODA.



**Scheme 2.** Synthesis of PEKI-C (**a–e**) from phenolphthalein, 4,4'-difluorobenzophenone, and/or 4,4'-bis(4-fluorophthalimido)diphenyl ether.

**Table 1**  
Units in the polymer chain and chemical shift of carbon atoms.

| Unit type | Units in the polymer chain | Chemical shift ( $\delta$ /ppm)                    |
|-----------|----------------------------|--|
| IPI       |                            | $C_{2'} = 166.80$<br>$C_{3'} = 166.65$             |
| KPI       |                            | $C_1 = 193.58$<br>$C_2 = 166.80$<br>$C_3 = 166.64$ |
| KPK       |                            | $C_{1'} = 193.54$                                  |



**Fig. 2.**  $^{13}\text{C}$  NMR spectra of the PEKI-C (**a–e**).

good solubility of these polymers could also be explained by the presence of aromatic ether linkages that increased the flexibility of the polymer backbone [24–35]. Meanwhile, copolymerization is usual but an effective method to enhance the solubility. Because the addition of the second component generally disrupted the regularity of polymer chain, and consequently weakened the inter-chain interactions [41].

### 3.3.2. Thermal properties

The thermal decomposition and stability of the PEKI-C were evaluated by TGA and DSC. The results were shown in Table 3. All data were obtained from the PEKI-C powders. As presented in Fig. 3, the  $T_g$  values were from 221 °C to 278 °C, and arranged in the order of **a** < **b** < **c** < **d** < **e**, which presented a general law that  $T_g$  values increased with increasing the content of phthalimide unit in the polymer backbone. This phenomenon was because the five-member heterocyclic phthalimide unit was much more rigid and had stronger inter-chain interactions than benzophenone unit.

As shown in Table 3, the  $T_{5\%}$  values of PEKI-C (**a–e**) in nitrogen stayed in the range 472–495 °C, and the  $T_{5\%}$  values in air were in the range 466–481 °C.

### 3.3.3. Mechanical properties

The mechanical properties of PEKI-C (**a–e**) films are listed in Table 3. The PEKI-C films about 20  $\mu\text{m}$  thick exhibited good mechanical properties with tensile strengths of about 100 MPa, elongations at break of more than 9.7%, and tensile moduli of more than 2.2 GPa. It is noted that the tensile strengths, elongations at break, and tensile moduli increased with increasing the content of the phthalimide unit, which effectively contributed to the inter-chain interactions [27,28].

### 3.3.4. Dynamic mechanical properties

The dynamic mechanical analysis spectra of PEKI-C (**a–e**) were presented in Fig. 4. The excellent storage moduli ( $E'$ ) almost completely maintained at about 2.3 GPa before reaching the

**Table 2**  
Solubility of PEKI-C.

| PEKI-C   | Ratio of II:III | Solvents <sup>a</sup> |     |     |      |      |     |     |                  |
|----------|-----------------|-----------------------|-----|-----|------|------|-----|-----|------------------|
|          |                 | CHCl <sub>3</sub>     | DCE | DMF | DMAc | DMSO | NMP | THF | <i>m</i> -cresol |
| <b>a</b> | 1:0             | ++                    | +-  | ++  | ++   | ++   | ++  | +-  | ++               |
| <b>b</b> | 3:1             | ++                    | ++  | ++  | ++   | ++   | ++  | ++  | ++               |
| <b>c</b> | 1:1             | ++                    | ++  | ++  | ++   | ++   | ++  | ++  | ++               |
| <b>d</b> | 1:3             | ++                    | ++  | ++  | ++   | ++   | ++  | ++  | ++               |
| <b>e</b> | 0:1             | ++                    | +-  | ++  | ++   | ++   | ++  | +-  | ++               |

Note Key: The qualitative solubility was tested with 10 mg samples in 1 mL solvent. ++, fully soluble at room temperature; +-, partially soluble or swelling on heating; -, insoluble.

<sup>a</sup> DCE, dichloroethane; DMF, *N,N*-dimethylformamide; DMAc, *N,N*-dimethylacetamide; DMSO, dimethyl sulfoxide; NMP, *N*-methyl-2-pyrrolidone; THF, tetrahydrofuran.

**Table 3**  
Thermal and mechanical properties of the PEKI-C.

| Polymer  | Ratio of II:III | $\eta_{inh}$ (dL/g) <sup>a</sup> | $T_g$ (°C)       |                   | $T_{5\%}$ (°C) <sup>d</sup> |        | Char yield <sup>e</sup> (%) | Strength at break (MPa) | Tensile moduli (GPa) | Elongation at break(%) |
|----------|-----------------|----------------------------------|------------------|-------------------|-----------------------------|--------|-----------------------------|-------------------------|----------------------|------------------------|
|          |                 |                                  | DSC <sup>b</sup> | DMTA <sup>c</sup> | In N <sub>2</sub>           | In air |                             |                         |                      |                        |
| <b>a</b> | 1:0             | 0.40                             | 221              | 218               | 472                         | 466    | 52.15                       | 73                      | 2.2                  | 9.7                    |
| <b>b</b> | 3:1             | 0.41                             | 249              | 243               | 481                         | 474    | 52.31                       | 95                      | 2.4                  | 10.2                   |
| <b>c</b> | 1:1             | 0.42                             | 262              | 257               | 487                         | 476    | 52.86                       | 108                     | 2.5                  | 11.3                   |
| <b>d</b> | 1:3             | 0.39                             | 271              | 269               | 493                         | 479    | 53.23                       | 116                     | 2.6                  | 11.9                   |
| <b>e</b> | 0:1             | 0.40                             | 278              | 275               | 495                         | 481    | 53.59                       | 124                     | 2.8                  | 12.8                   |

<sup>a</sup> Inherent viscosity measured with 0.5 g/dL at 30 °C in DMAc.

<sup>b</sup> Obtained from DSC at a heating rate of 20 °C/min in nitrogen.

<sup>c</sup> Obtained from DMTA at heating rate of 3 °C/min at 1 Hz.

<sup>d</sup>  $T_{5\%}$  = 5% weight loss temperature (obtained by TGA at a heating rate of 10 °C/min in nitrogen or air).

<sup>e</sup> Residual weight (%) at 800 °C in nitrogen.

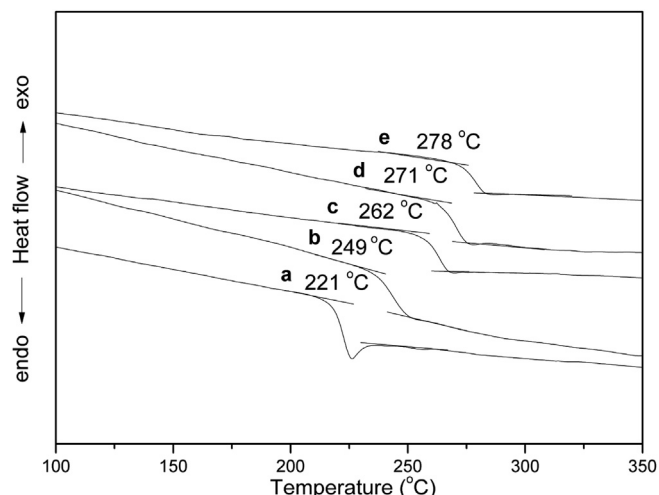
corresponding  $T_g$ s. The peak temperature in the  $\tan\delta$  curves was regarded as the glass transition temperature, the  $T_g$  of these PEKI-C arranged in the order: **a** (218 °C) < **b** (243 °C) < **c** (257 °C) < **d** (269 °C) < **e** (275 °C), which were slightly lower than that measured by DSC.

### 3.3.5. Optical properties

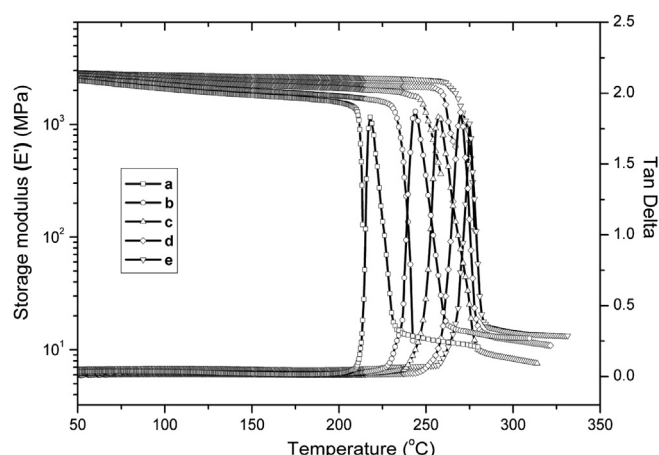
Optical transparency of the PEKI-C (**a–e**) films were evaluated by their physical appearance and UV–vis spectra. Fig. 5 shows the optical photographs of these films. It is noted that these films were transparent and essentially colorless, which was significantly different from the deep yellow or brown color of traditional aromatic polyimide films from pyromellitic dianhydride (PMDA) and 4,4'-oxydianiline (ODA).

Typical UV–visible spectra of these films are illustrated in Fig. 6. The cut-off wavelengths (absorption edge,  $\lambda_0$ ) and the

transmittance at 400, 450, 500 nm from the UV–visible spectra are summarized in Table 4. As expected from the bulky cardo phthalide groups' nature, all of the films exhibited excellent optical transparency, which gave the UV cutoff wavelengths shorter than 368 nm and transmittance at 450 nm higher than 81%. It is sharply contrasted with the typical aromatic polyimide film derived from PMDA and ODA, which showed deep yellow color and exhibited  $\lambda_0$  of 445 nm and transmittance at 450 nm of 2%. The excellent optical transparency of these films was attributed to the incorporation of the bulky cardo phthalide groups in the polymer structure, which inhibited close packing, thereby increasing the free volume among the molecular chains and suppressing the inter- and intramolecular charge transfer interactions effectively [27,28]. As comparing the coloration of these films, it is interestingly observed that optical transparency slightly increased with decreasing the content of phthalimide unit in the polymer backbone.



**Fig. 3.** DSC curves of the PEKI-C (**a–e**) in nitrogen at a heating rate of 20 °C/min.



**Fig. 4.** Dynamic mechanical analysis spectra of the PEKI-C (**a–e**).



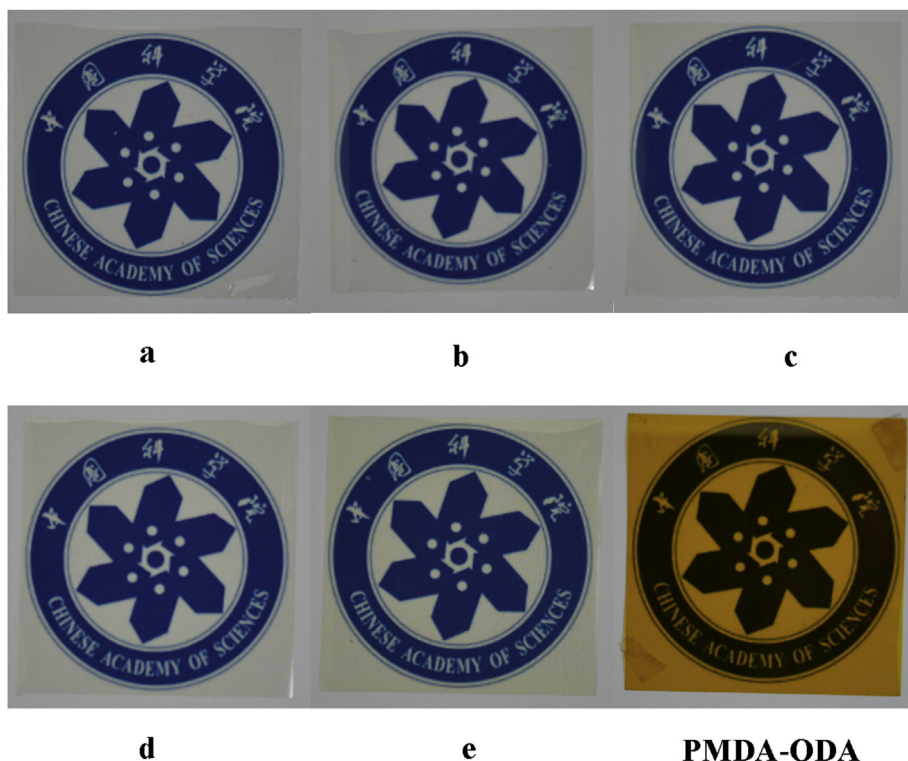


Fig. 5. Photographs of the PEKI-C (a–e) films.

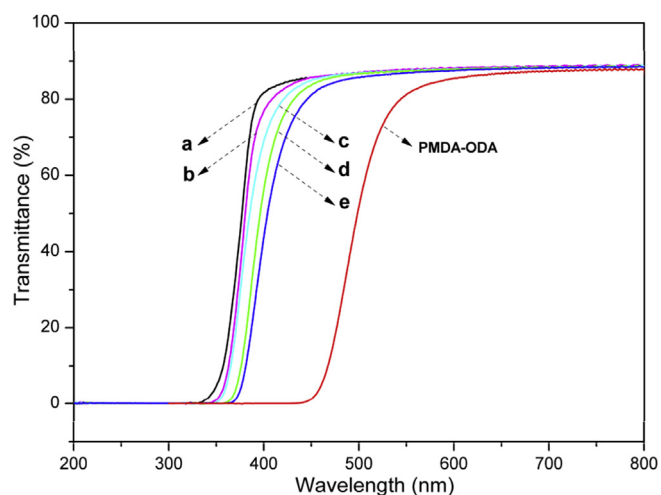


Fig. 6. UV-vis spectra of the PEKI-C (a–e) films.

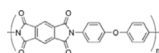
**Table 4**  
Optical properties of the PEKI-C films.

| PEKI-C                | d (μm) | $\lambda_0$ (nm) <sup>a</sup> | $T_{400}$ (%) <sup>b</sup> | $T_{450}$ (%) <sup>b</sup> | $T_{500}$ (%) <sup>b</sup> |
|-----------------------|--------|-------------------------------|----------------------------|----------------------------|----------------------------|
| <b>a</b>              | 16     | 336                           | 82                         | 86                         | 87                         |
| <b>b</b>              | 15     | 347                           | 77                         | 85                         | 87                         |
| <b>c</b>              | 13     | 351                           | 69                         | 84                         | 86                         |
| <b>d</b>              | 16     | 362                           | 57                         | 83                         | 86                         |
| <b>e</b>              | 21     | 368                           | 44                         | 81                         | 85                         |
| PMDA-ODA <sup>c</sup> | 19     | 445                           | 0                          | 2                          | 52                         |

<sup>a</sup>  $\lambda_0$ : UV cut-off wavelength.

<sup>b</sup>  $T_{400}$ ,  $T_{450}$ ,  $T_{500}$ : transmittance at 400, 450, 500 nm, respectively.

<sup>c</sup> PMDA-ODA with the chemical structure as follows.



It is interestingly observed that  $\lambda_0$  decreased in the order of **e** > **d** > **c** > **b** > **a**, while the transmittance at 400 nm (from 44% to 82%) and 450 nm (from 81% to 86%) increased in the order of **e** < **d** < **c** < **b** < **a**. This phenomena was probably attributed to the decreasing content of the five-member heterocyclic phthalimide unit, which effectively contributed to the inter- and intramolecular charge transfer interactions [27,28].

### 3.3.6. XRD

As shown in Fig. 7, morphological structures of PEKI-C (a–e) were evaluated by wide-angle X-ray diffraction measurements. The XRD spectrum of the Kapton<sup>®</sup> polyimide produces three peaks at 15.10°, 22.44° and 26.12° with the most intense peak appearing at

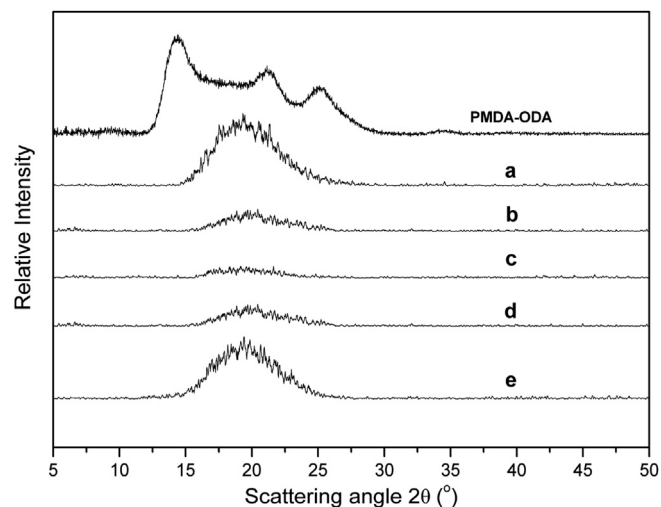


Fig. 7. XRD patterns of the PEKI-C (a–e) films.

**Table 5**  
Rheological properties of the PEKI-C.

| PTEIs    | $\eta_{inh}$ (dL/g) <sup>a</sup> | $M_n$ (g/mol) | $M_w$ (g/mol) | $M_w/M_n$ | Minimum melt viscosity | $MI^b$ (g/10 min) |
|----------|----------------------------------|---------------|---------------|-----------|------------------------|-------------------|
| <b>a</b> | 0.40                             | 9800          | 20,200        | 2.04      | 4403 Pa·s at 342 °C    | 4.6               |
| <b>b</b> | 0.41                             | 10,800        | 19,700        | 1.82      | 5395 Pa·s at 345 °C    | 4.3               |
| <b>c</b> | 0.42                             | 11,000        | 21,300        | 1.93      | 6146 Pa·s at 348 °C    | 3.2               |
| <b>d</b> | 0.39                             | 9500          | 18,600        | 1.95      | 7653 Pa·s at 350 °C    | 1.3               |
| <b>e</b> | 0.40                             | 10,300        | 21,100        | 2.06      | 8975 Pa·s at 352 °C    | 0.9               |

<sup>a</sup> Inherent viscosity measured at a concentration of 0.5 g/dL in DMAc at 30 °C.

<sup>b</sup> Measured at a load of 12.5 kg at 330 °C.

15.10°. While, most of the PEKI-C films had typical Gaussian distribution curve, broad and amorphous, suggesting that all the PEKI-C (**a–e**) were amorphous. The amorphous nature of these cardo polyimides could be attributed to the introduction of large-volume phthalide groups, which resulted in loose chain packaging and aggregation. Meanwhile, copolymerization effectively disrupted the regularity of polymer main chain.

### 3.3.7. Rheological behavior

The melt index and rheological properties of PEKI-C (**a–e**) were studied in detail. All the PEKI-C (**a–e**) discussed were obtained from the PI powders, and the inherent viscosities were controlled to the similar molecular weight about 0.40 dL/g by end capping agent of *N*-phenyl-4-fluorophthalimide. As presented in Table 5, the  $M_n$  of this series PEKI-C (**a–e**) was about 10,000 g/mol, meanwhile  $M_w$  was near about 20000 g/mol. The complex viscosity was measured on the rotational rheometer over the range of 300–400 °C. The data were collected at a frequency of 1 Hz, a strain of 3%, and a heating rate of 3 °C/min. The complex viscosity means the viscosity of melted polymers, it is related to the melt processability. Fig. 8 displays the rheological behaviors of PEKI-C (**a–e**). The complex viscosities dramatically decreased above  $T_g$  for all the polymers, which was consistent with the phenomena of their films softening rapidly in DMTA test. It was found that the complex viscosity of PEKI-C (**a**) was the lowest among these polymers over a very wide temperature range and the minimum complex viscosity was about 4403 Pa s at 342 °C.

Furthermore, as summarized in Table 5, the minimum complex viscosity of PEKI-C (**a–e**) decreased with decreasing the content of phthalimide unit, and arranged in the order: **e** > **d** > **c** > **b** > **a**, which was consistent with the trend of MI tested by SRZ 400E molten index instrument. This rheological behavior was because the five-member heterocyclic phthalimide unit was much more

rigid and had stronger inter-chain interactions than benzophenone unit.

## 4. Conclusion

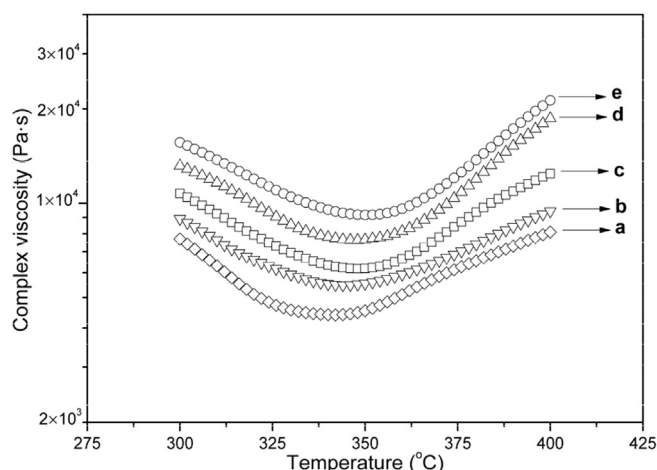
A series of cardo poly(ether ketone imide)s (PEKI-C) (**a–e**) containing large-volume phthalide groups were synthesized and characterized. All cardo polymers had excellent solubility in ordinary organic solvents, which could be explained by the presence of large-volume cardo phthalide groups. The  $T_g$  values increased from 221 to 278 °C with increasing the content of phthalimide unit in the polymer backbone. The dynamic mechanical analysis illustrated that excellent storage moduli almost completely maintained before reaching the corresponding  $T_g$ s. The minimum complex viscosity decreased with decreasing the content of phthalimide unit, and arranged in the order: **e** > **d** > **c** > **b** > **a**. The good optical transparency of these PEKI-C (**a–e**) films was associated with the incorporation of the large-volume cardo phthalide groups into the polymer backbone, which inhibited close packing, thereby increasing the free volume among the molecular chains and reducing the interchain interactions. These data demonstrated that this kind of novel cardo poly(ether ketone imide)s endowed with good solubility, high thermal stability, and good optical transparency can be served as high performance optical materials, where the properties could be adjusted by controlling the ratio of 4,4'-bis(4-fluorophthalimido)diphenyl ether/4,4'-difluorobenzophenone.

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**Fig. 8.** Rheological behavior of the PEKI-C (**a–e**) as a function of temperature.

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